

SOME EFFECTS OF ALKALI SORPTION AND CHLORINE  
OXIDATION ON A CORNSTARCH

by

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## INTRODUCTION

The modification of starch to increase its capacity to form a glutinous paste is of primary interest from both theoretical and industrial points of view. The industrial chemist is primarily interested in obtaining a product of increased industrial value. The research chemist, on the other hand, strives through different types of modification to gain an insight into the structure of the starch granule.

Work in this laboratory on the chlorine oxidation of cornstarch was begun by Paine (6). He developed a procedure which gave improved control over the resulting changes. In the course of his work, it was found that the base sorbed by a starch was of two types, that available to titration by acid, and that unavailable. On the basis of the specificity of this sorption, the latter seemed to offer a good measure of control over oxidative effects. Accordingly, Paine elected to study the effects on starch of the reaction of chlorine with sodium hydroxide sorbed at specific sites. The glutinous quality of the starch pastes produced by this method first increased and then decreased with increasing quantities of reactants.

Since the glutinous quality developed by Paine's procedure fell far short of the limits of glutinous character possessed by some native starches, further work was pursued that involved the reaction of chlorine with the base sorbed by a starch which is available to acid titration.

In the present study the investigation of the oxidation of a cornstarch by chlorine was continued. It was hoped that a process would result by which a controlled increase in the glutinous character of the starch could be obtained without structural damage and the consequent adverse effects on pasting characteristics.

#### LITERATURE SURVEY

The first observation of the oxidation of starch was by Justus Liebig in 1829 (Kerr,4). He noted that starch was affected by the action of chlorine or chlorous acid. Since this early beginning, work has been carried out using a wide variety of oxidizing agents. These include: permanganates, dichromates, hydrogen peroxide, fluorine, manganese dioxide, perborates, persulfates, hypochlorites, and oxygen (5).

Felton, et.al. (3) found that the oxidation of starch is of four types. The oxidation of aldehyde groups to carboxyl groups, the oxidation of primary alcohol groups to carboxyl groups, the oxidation of secondary alcohol groups to ketone groups, and the oxidation of glycol groups to carboxyl groups. All four types of oxidation may occur concurrently, although some methods are more selective than others.

In a study of the properties of hypochlorite oxidized starches, Farley and Hixon (2) found that rigidity, gel strength, and turbidity decrease in proportion to the amount



of oxidizing agent used. They concluded that oxidation is localized in the regions between radial starch crystallites. Once begun, the oxidation continues in the same region and the oxidizing agent penetrates deep into the granule.

Many authors have noted that oxidized starches still have practically the same granular structure, are insoluble in cold water, and show the characteristic color reaction with iodine.

#### EXPERIMENTAL PROCEDURE

The apparatus used in these experiments consisted of a six necked flask, a pH meter and a water bath where the temperature could be controlled to variations of  $1^{\circ}\text{C}$ . The pH meter was a Leeds and Northrup pH indicator number 7664-AI provided with a glass electrode and a calomel reference electrode. The flask was the reaction vessel and was fitted with ground glass joints for a thermometer, a stirrer which was attached to a cone drive stirring motor, and a gas diffuser that extended into the slurry. The electrodes of the pH meter were inserted into two of the remaining necks. The sixth neck was reserved for the addition of reagents and as a gas outlet.

The standard procedure for the oxidation consisted of placing 150 grams, dry weight, of cornstarch and 563 ml. of distilled water in the six necked flask. The flask then was placed in a water bath at the desired temperature, and allowed

to slurry for one hour with nitrogen gas passing through the slurry. After this pretreatment period, the pH of the slurry was noted and the cycling started. A cycle consisted of a period of time during which the reagents were added, the reaction period, and the period during which the pH was re-established to a value of seven. Two different procedures were used in carrying out this cycling. One consisted of removing the starch from the flask between cycles and washing it before starting another cycle. In the other procedure the cycles were carried out in rapid order without removing the starch from the flask. In this way the reaction time was held to a minimum.

At the completion of the pretreatment period, when using the rapid cycle method, normal sodium hydroxide solution was added to the slurry until a desired pH was attained, or a definite quantity of base had been added. Immediately, saturated chlorine water at a temperature of 25° C. was added in such a quantity as to give a mole to mole ratio between the added base and molecular chlorine. The slurry was allowed to react for one minute, after which a pH of seven was established by adding normal base. This was the end of the first cycle. If further cycles were desired, the required amount of base was added immediately, followed by the addition of the corresponding amount of saturated chlorine water. The slurry again was allowed to react for one minute before the pH was re-established at seven, thus ending the second cycle. This procedure was repeated for the number of cycles desired.

After the final cycle the slurry was allowed to react for five minutes before bringing the pH back to a value of seven where it was maintained for several minutes. This ended the reaction period.

When using the reaction procedure with washing between cycles, the reaction time after addition of the base and chlorine was five minutes. The pH then was brought to seven and maintained there for several minutes. The starch slurry was removed from the flask and washed until the washings no longer gave a precipitate with a silver nitrate solution. This ended one cycle. The filter cake was reslurried with 500 ml. of water, 63 ml. being retained by the filter cake. The pretreatment period for the second and succeeding cycles was reduced to thirty minutes. The oxidation then was carried out in the same manner as in the first cycle for as many cycles as was desired.

After the reaction period, the flask was removed from the water bath and the slurry filtered by suction. The filter cake was washed with water until the hypochlorite odor was no longer evident and the washings were free from chloride ion. The sample was air dried until it had reached the equilibrium moisture level. The starch then was ground to pass through a sixty mesh screen. The oxidized starches were all designated as RH- followed by the experiment number.

The samples prepared in this way were evaluated for their pasting characteristics. A viscosity record of each sample



was obtained using a rotating cylinder viscometer (1) that has been developed to measure continuously the changes in viscosity which take place in starch pastes throughout one or more cycles of temperature. The data obtained from this viscosity record includes a hot peak viscosity, a cold paste viscosity, and a gel strength. These quantities are designated in the tables as  $W_1$ ,  $W_2$ , and GS, respectively. Two other quantities are derived from these values. One index,  $W_2/W_1$ , is a measure of the glutinous character of the starch. A value of one represents an extreme of glutinous character. The index,  $\frac{(GS-W_2)100}{W_2}$ , bears a qualitative relation to the paste length.

#### EXPERIMENTAL RESULTS

The term unimolecular layer is used throughout this paper to define an amount of sodium hydroxide sorbed by the starch. One unimolecular layer is defined as that amount of sodium hydroxide required to cover a given weight of cornstarch having a specific surface of 3000 square centimeters per gram. For 150 grams of cornstarch, 2.5 ml. of normal sodium hydroxide furnishes one layer of sorbed base.

Cornstarches used in this study were designated CS-12, SC1, SC1-E, CS-14, and CS14-A. The starch CS-12 was a commercially milled cornstarch while the others were milled in our laboratory. The milling technique used in preparing



these starches was essentially the same as is used commercially except that the sulfur dioxide steep was omitted. Cornstarch SC1 was milled in 1947, while CS-14 was milled in 1953. Starch SC1-E was a portion of starch SC1 that had been solvent extracted with methanol according to the Schoch procedure (7). Cornstarch CS14-A was a sample of CS-14 which had been extracted with ammonia. The viscosity data for these starches are found in Table 1.

Table 1. Paste characteristics of starches

Starch	$W_1$	$W_2$	$W_2/W_1$	GS	$\frac{(GS-W_2)100}{W_2}$
CS-12	404	1095	2.71	2605	137.9
SC1	395	1586	4.02	2842	79.19
SC1-E	328	1377	4.20	1810	31.45
CS-14	376	1359	3.61	1149	-15.45
CS14-A	368	1280	3.48	1843	44.77

Preliminary experiments as to the nature of the sorption of sodium hydroxide by cornstarch showed that most of the base is available to titration if the time of sorption is kept relatively short.

Since two possible methods of carrying out the cycling process were available, an attempt was made to determine the effects of oxidation by each method. The oxidation was carried out at pH values of 8, 9, 10, and 11 for one through three cycles at a temperature of 25° C. The oxidized samples of CS-12 which were prepared by the method of washing between

cycles were designated RH-08, -11, -13, and -15 corresponding to the following conditions respectively: a pH of 9 and 2 cycles; a pH of 11 and 2 cycles; a pH of 9 and 3 cycles; and a pH of 11 and 3 cycles. The oxidized starches that had no washing between cycles were designated RH-29, -27, -30, and -28 and corresponded respectively to the same conditions as above. Also, a sample designated as RH-31 was oxidized at a pH of 9 for 4 cycles without washing between cycles. The pasting data for these samples are shown in Table 2.

Table 2. Paste characteristics of starch products

Starch	Layers	$W_1$	$W_2$	$W_2/W_1$	GS	$\frac{(GS-W_2)100}{W_2}$
RH-08	1.90	441	1295	2.94	2095	61.78
11	5.55	480	1138	2.36	1764	55.59
13	3.62	508	1302	2.56	2898	122.6
15	8.57	396	916	2.37	1712	86.90
27	8.60	451	895	1.98	1636	82.79
28	16.40	430	932	2.17	1584	69.96
29	2.28	676	1270	1.88	2153	69.54
30	4.50	563	1211	2.15	2437	101.2
31	7.41	525	1085	2.07	1776	63.69

The oxidized starches prepared by the rapid cycling method displayed much higher hot paste viscosities than those prepared with washing between cycles. These samples also had made more progress toward the desired glutinous condition. Because of these facts, the method of oxidation without washing between cycles was used throughout the remainder of the experiments whenever a cycling procedure was used.

To determine the effects of temperature on the oxidation, temperatures above and below the 25° C. previously used were employed. Temperatures of 60° and above could not be used since gelatinization of the sample occurred during the oxidative process. A temperature of 59° caused no gelatinization if the quantity of base did not exceed five layers. This would not permit the effects of higher concentrations of base to be explored. By lowering the temperature to 55° both gelatinization and concentration difficulties could be avoided. Another temperature selected was 4° which approaches the minimum usable temperature at which liquid water can exist. The oxidation of samples of CS-12 at these temperatures was carried out using the same pH values as before for one through three cycles. The samples that were oxidized at a temperature of 4° and a pH of 10 were designated RH-83, -84, and -85 corresponding to 1, 2, and 3 cycles, respectively. Those oxidized at a pH of 11 for 1, 2, and 3 cycles were designated RH-75, -77, and -79. RH-78 was oxidized at a pH of 9 for 3 cycles also at a temperature of 4°. The samples oxidized at 55° at a pH of 9 were RH-47 and -64 corresponding to two and three cycles respectively. The two and three cycle oxidized starches at a pH of 10 are RH-48 and -65, respectively. RH-40 was oxidized at a pH of 10.5 for one cycle at a temperature of 55°. The pasting data for these samples are shown in Table 3.

The samples oxidized at 55° C. in general showed an increase in hot paste viscosity, but the cold paste viscosity



Table 3. Paste characteristics of starch products

Starch	Temp.	Layers	$W_1$	$W_2$	$W_2/W_1$	GS	$\frac{(GS-W_2)100}{W_2}$
RH-40	55	3.20	553	1415	2.56	2555	80.56
47	55	2.62	715	1358	1.90	2443	79.90
48	55	4.98	467	1122	2.40	1869	66.57
64	55	4.60	534	1133	2.12	2011	77.57
65	55	8.37	414	970	2.34	2878	196.7
75	4	2.80	671	1140	1.70	1647	44.48
77	4	5.96	552	920	1.67	1842	100.2
78	4	2.26	443	978	2.21	2616	167.5
79	4	15.40	449	995	2.22	1992	100.2
83	4	1.26	428	1120	2.62	2581	130.5
84	4	3.22	426	1242	2.92	2346	88.89
85	4	6.43	533	1140	2.14	2092	83.51

likewise had increased. The overall increase in glutinous character, therefore, was very slight. On the other hand, the samples oxidized at 4° had made more progress toward the desired glutinous state than samples obtained at either 55° or 25°.

A further attempt was made to determine the optimum reaction temperature. Three samples of GS-12 were oxidized at 55°, 25°, and 4° C. using an alkali concentration of four layers for one cycle. The oxidized starches were designated RH-69, -71, and -67, respectively. These three oxidized starches all showed an increase in glutinous character as measured by the paste index. However, the sample oxidized at 4° had the highest hot paste viscosity of the three and seemed to have the greatest possibility of attaining the desired glutinous state upon further treatment. The effect of low temperature hydration, the treatment of starch slurries

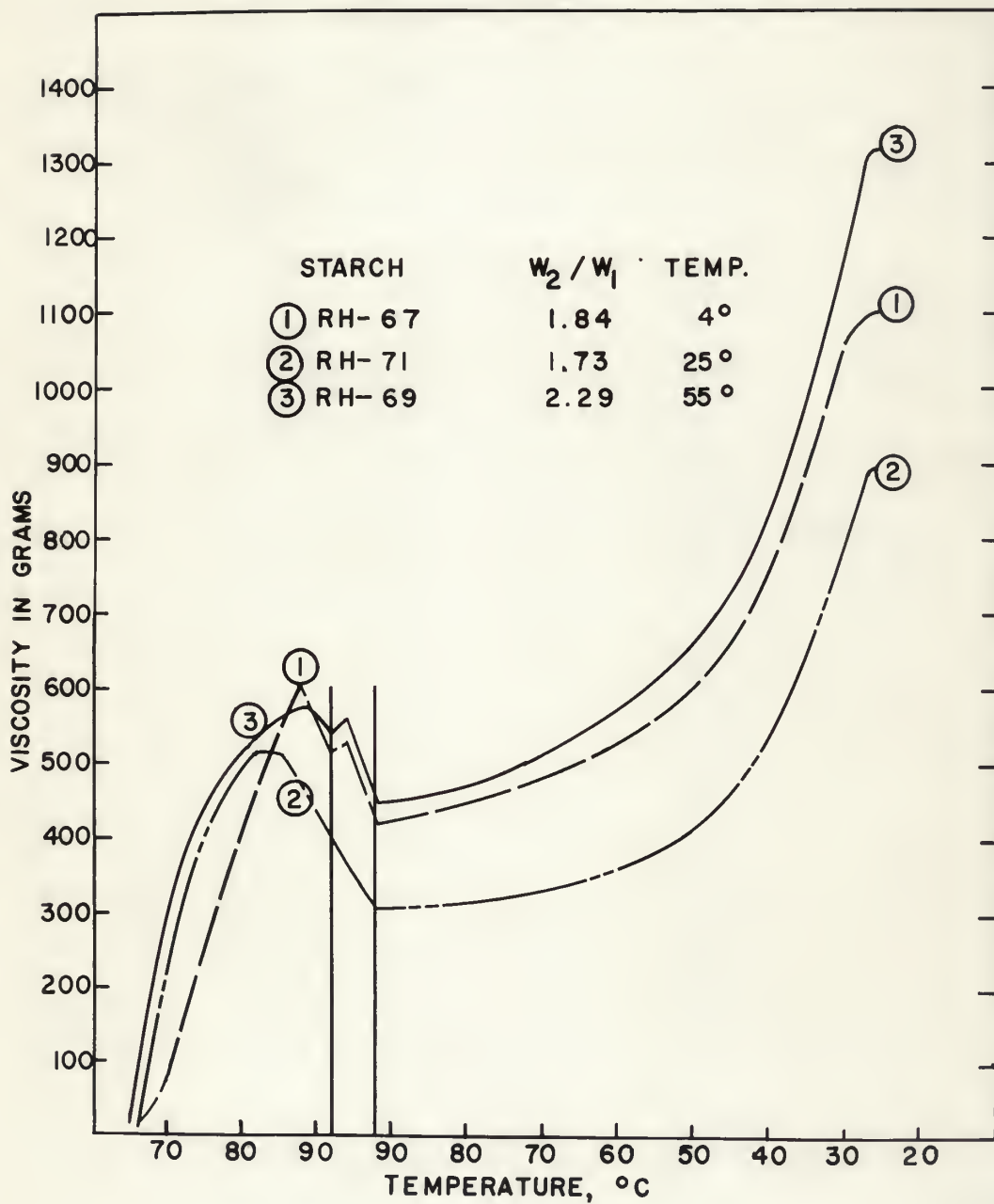


Fig. 1. The effect of temperature.

for prolonged periods at just below the gelatinization temperature, on samples oxidized in this manner was also determined. Oxidized starches were slurried for one hour at 55° after the oxidation had been carried out. The hydrated samples were designated RH-70, -72, and -68 corresponding to an oxidation temperature of 55°, 25°, and 4°, respectively. An oxidized starch, designated as RH-73, was prepared by hydrating 150 grams of CS-12 for one hour at 55° before oxidizing the starch at 4° in the presence of four layers of base. The hydration before oxidation gave a definite decrease in glutinous character while the effect of hydration after oxidation was uncertain. The pasting data for this group of oxidized starches are given in Table 4.

Table 4. Paste characteristics of starch products

Starch	Temp.	$W_1$	$W_2$	$W_2/W_1$	GS	$\frac{(GS-W_2)100}{W_2}$
RH-67	4	602	1105	1.84	1542	29.55
68	4	605	1094	1.81	1839	68.10
69	55	579	1319	2.29	2854	116.4
70	55	610	1379	2.26	2398	42.49
71	25	516	893	1.73	2058	130.5
72	25	586	1078	1.84	2364	119.3
73	4	554	1102	1.99	2257	104.8

An attempt was made to increase the glutinous character of a cornstarch by carrying out the oxidation at pH values of eleven and above using one cycle. This procedure gave oxidized starches with a desired decrease in index but the hot paste viscosity also had decreased.



A slightly different oxidation procedure was used to prepare several oxidized starches. It consisted of adding the base and chlorine water simultaneously. The rates of addition were controlled to maintain a constant pH value during the oxidation. This method gave high hot paste viscosities but the overall glutinous character of the oxidized starches was not as good as was obtained by some of the other methods employed.

The effects of oxidation on various cornstarches was determined. Cornstarches CS-12, SC1, SC1-E, CS-14, and CS14-A were all oxidized at a temperature of 4° C. using four layers of base. The oxidized starches were designated RH-67, -SC1, -SC1-E, -80, and 81 corresponding respectively to the above starches. The pasting data for these samples are found in Table 5. These pasting data show that the commercial cornstarch responded best to the oxidation, and their properties showed an increase toward a more glutinous state. The solvent extracted starch, RH-SC1-E, was completely inhibited in its ability to respond to oxidation. The oxidation of the starches which had not been treated with sulfur dioxide, gave an increase in hot paste viscosity but the overall glutinous character of the starch had not made as much progress as the commercial cornstarch.

The resistance to oxidation of starches that had not been treated with sulfur dioxide is further demonstrated by a series of samples of CS14-A which were oxidized in the

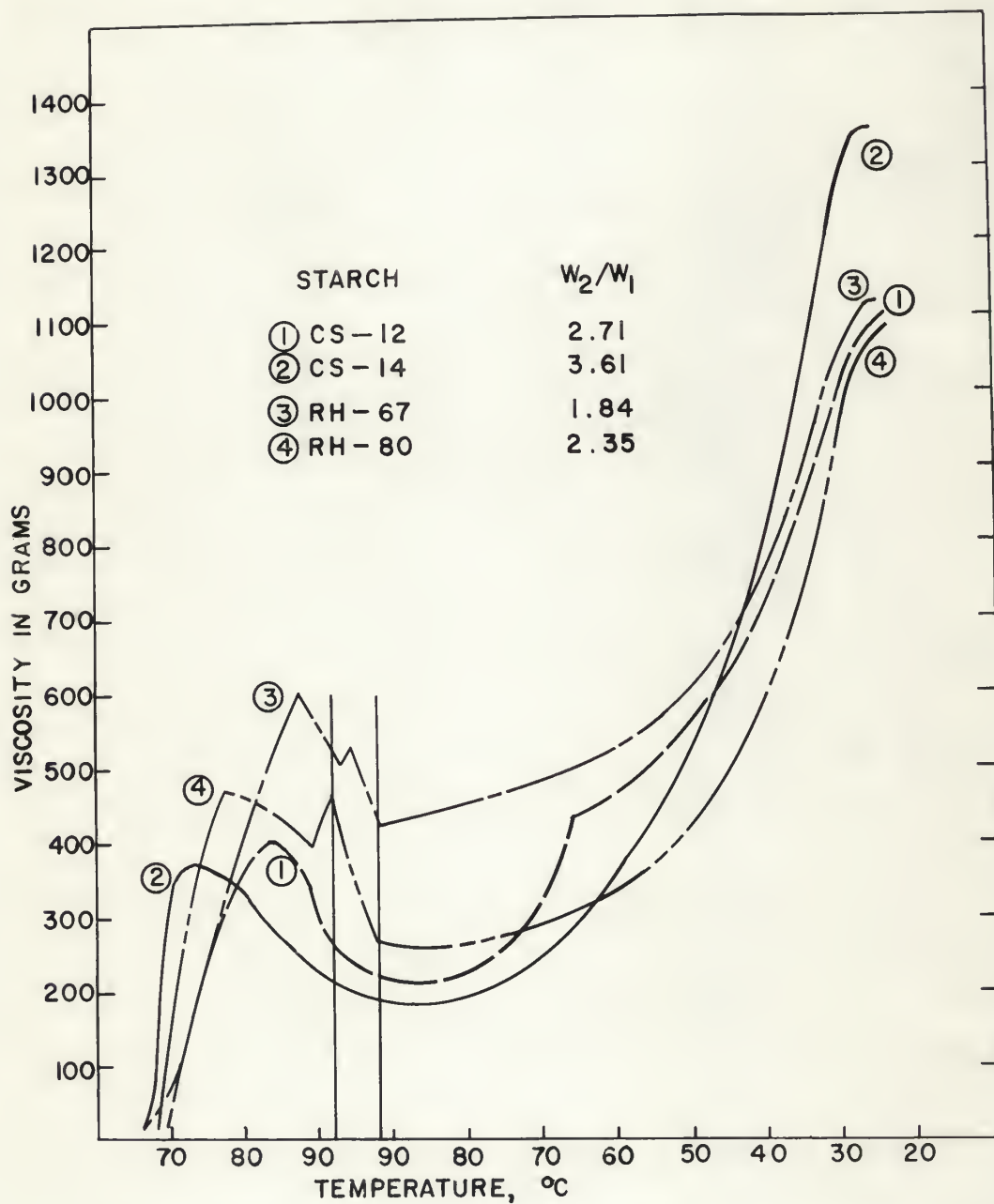


Fig. 2. Effects of oxidation on different starches.

Table 5. Paste characteristics of starch products

Starch	$W_1$	$W_2$	$W_2/W_1$	GS	$\frac{(GS-W_2)100}{W_2}$
RH-67	602	1105	1.84	1542	29.55
SC1	607	1690	2.78	2575	52.36
SC1-E	310	1558	5.03	2203	41.40
80	468	1100	2.35	1387	26.09
81	491	1193	2.43	1938	54.07

presence of varying amounts of base. The oxidized starches were designated RH-89, -81, -87, -88, and -86 corresponding to oxidation at 4° C. using 2, 4, 6, 8, and 10 layers of base, respectively. A two cycle sample, RH-90, also was prepared using eight layers per cycle or a total of sixteen layers of normal sodium hydroxide. The pasting data for these starches are found in Table 6. None of these oxidized starches gave the increase in hot paste viscosity shown by a commercial cornstarch when treated under similar conditions. These starches also failed to show as great an increase in glutinous characteristics as a commercial cornstarch.

Table 6. Paste characteristics of starch products

Starch	Layers	$W_1$	$W_2$	$W_2/W_1$	GS	$\frac{(GS-W_2)100}{W_2}$
RH-81	4	491	1193	2.43	1838	54.07
86	10	530	1480	2.79	1863	25.88
87	6	527	1203	2.27	1806	50.12
88	8	480	887	1.85	1085	22.32
89	2	385	1273	3.31	1510	18.62
90	16	469	1173	2.50	1525	30.01



In order to definitely establish the effect of the sulfur dioxide steep on a cornstarch, four 200 gram samples of cornstarch CSL4-A were steeped for 48 hours at a temperature of 49° C. with varying amounts of sulfur dioxide. The samples were designated 0.1% SO<sub>2</sub>, 0.2% SO<sub>2</sub>, 0.3% SO<sub>2</sub>, and 0.4% SO<sub>2</sub> and correspond to the amount of sulfur dioxide used in the steep water. A portion of each of these steeped samples was oxidized at a temperature of 4° in the presence of four layers of base. The oxidized samples were designated RH-91, -92, -93, and -94 corresponding to the amount of sulfur dioxide from 0.1 per cent to 0.4 per cent used. The viscosity data for these samples are found in Table 7.

Table 7. Paste characteristics of starch products.

Starch	$W_1$	$W_2$	$W_2/W_1$	GS	$\frac{(GS-W_2)100}{W_2}$
0.1% SO <sub>2</sub>	373	1129	2.83	1710	51.46
0.2% SO <sub>2</sub>	277	797	2.88	1058	34.13
0.3% SO <sub>2</sub>	184	568	3.09	849	49.47
0.4% SO <sub>2</sub>	168	490	2.92	921	87.96
RH-91	505	1410	2.79	1177	-16.52
92	406	970	2.39	817	-15.77
93	102	177	1.74	274	54.80
94	108	200	1.85	460	130.0

An amount of sulfur dioxide corresponding to 0.1 per cent by weight did not decrease the pasting capacity of the cornstarch although it displaced the peak of the hot viscosity toward a higher temperature. Also, the hump in the early part of the cooling curve indicating increased structuralization

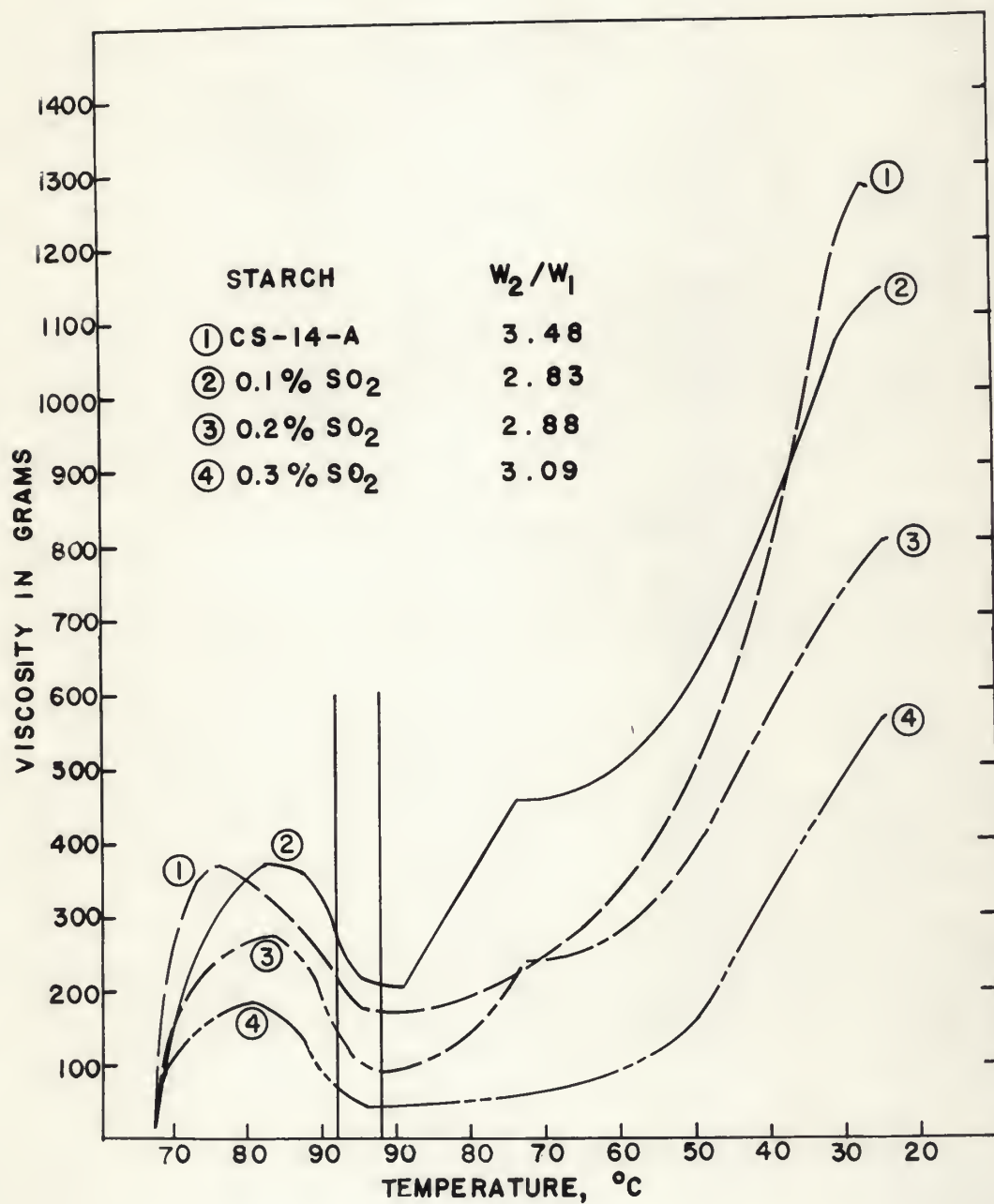


Fig. 3. Effect of sulfur dioxide.

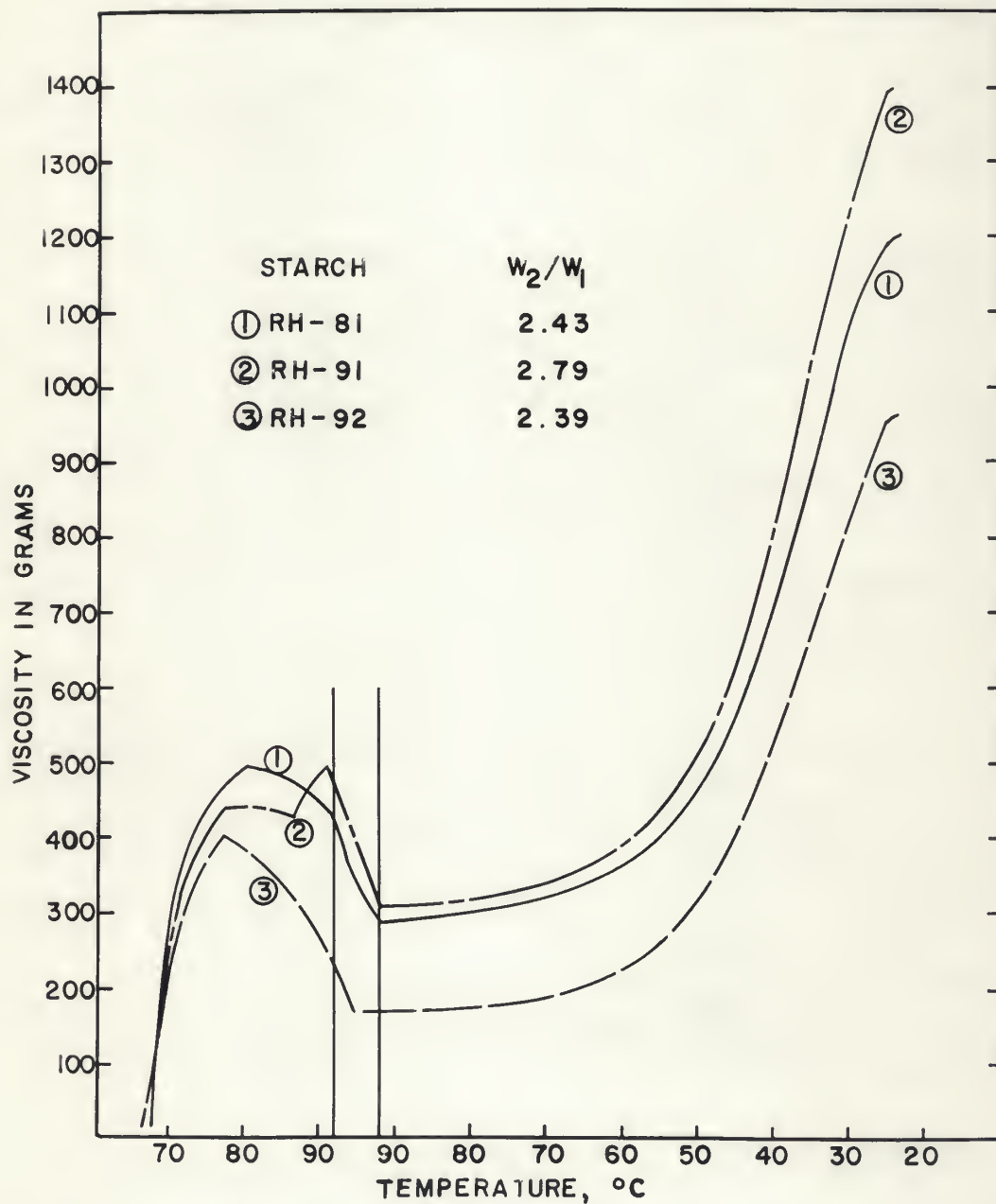


Fig. 4. Oxidation of sulfur dioxide treated starches.



was exaggerated. This hump is common in commercial starches but is very slight in the pasting curves of starches prepared without the use of sulfur dioxide. Larger quantities of the reagent gave appreciable decreases in the pasting capacity of the starch. The effect was so pronounced that the sample treated with 0.3 per cent sulfur dioxide gave a very thin bodied paste. Oxidation of the starches treated with 0.1 per cent and 0.2 per cent sulfur dioxide gave an increase in hot paste viscosity and decrease in the index similar to that obtained when a commercial cornstarch was oxidized. The more highly damaged starches were unable to respond desirably to oxidation.

Oxidized starches showed a definite lack of stability. The viscosity of an oxidized starch that had a high hot paste viscosity when originally determined was evaluated again after standing for eight months in a closed glass jar at room temperature. At this later time the oxidized starch had lost about 15 per cent of its hot paste viscosity. The pasting curve in general showed a number of irregularities indicating a general deterioration. After another eight month period the viscosity of the sample was determined again. By this time the rate of deterioration had slowed down and the starch showed only a slight further decrease in pasting capacity.

## DISCUSSION

The oxidation of cornstarch by this method in general failed to yield a product of the desired glutinous character. The most favorable conditions found for the oxidation were using four layers of base, which is 0.07 ml. of normal sodium hydroxide per gram of starch, a mole to mole reaction between chlorine and base, and a temperature of 4° C. These conditions consistently gave starch pastes that were intermediate in glutinous character.

In general the starch pastes produced had undesirable characteristics. For the most part they were short and quite cloudy. The cloudy appearance of the pastes is due to the linear material present in the pastes. It was evident that the amount of linear material increased with an increase in oxidation. This suggests that the oxidation proceeds in such a manner that the starch granule breaks up into more of the linear fraction than is isolated normally from a cornstarch paste.

The effect of temperature seemed to be twofold. First, there was a general randomization of the internal structure of the starch granule by a higher temperature. This should make possible a greater uptake of water in a given time and therefore a more glutinous state. This was not obtained since there was a general degradation of the oxidized bonds by heat. This allowed the general breakdown in the pasting

characteristics of the starch and helps to explain some of the irregularities that were observed in the pasting curves of some of the starches.

The effect of sulfur dioxide on a cornstarch appears to be somewhat the same as oxidation. It is a well known fact that upon aging, commercial cornstarches suffer a decrease in pasting capacity. It was pointed out that cornstarches milled without the use of sulfur dioxide did not decrease in pasting capacity over a period of several years. It seems reasonable to suppose that these starches will never be effected very much by age. This clearly indicates that sulfur dioxide is directly related to the aging of a commercial cornstarch. It previously was pointed out that oxidized starches retrograde in much the same manner only at a much faster rate. This increased rate could be due to a greater extent of damage to the starch during oxidation because of a much higher concentration of reagent. The direct effect of sulfur dioxide on an undamaged cornstarch has also been established. The effect of an increasing quantity of the reagent on the pasting ability of the starch is the same as oxidation. The quantity of sulfur dioxide used was a little greater than that used by industry since starch was used as the starting material instead of the whole grain. This allowed a slightly greater effect than is normally noted but the general pattern is the same. Therefore, it appears that commercially prepared cornstarch acts as a mildly oxidized starch.



The results of this study supports the findings of Paine (6) that a controllable procedure for the oxidation is possible. However, the reaction involves a breaking of bonds in the granule to the extent that it is objectionable. It has also been pointed out that commercial cornstarches have undergone structural changes which may have adverse effects on their response to subsequent treatments.

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The modification of starch to increase its capacity to form a glutinous paste is of primary interest from both the theoretical and industrial points of view. The starch selected for this study was cornstarch because of its industrial prominence. The modification was carried out by allowing chlorine to react with cornstarch which previously had been allowed to sorb sodium hydroxide.

Previous work on the chlorine oxidation of cornstarch indicated that the sorbed base was of two types, that available to acid titration and that unavailable. This study utilized the base available to titration. It was hoped that a reaction would result whereby a controlled increase in the glutinous character of the starch could be obtained without structural damage and the consequent adverse effects on pasting characteristics.

Oxidized starches were prepared by a number of related methods and the starches were evaluated for their pasting characteristics. In general, the pastes produced were short and quite cloudy. The most favorable conditions found for the reaction were using 0.07 ml. of normal sodium hydroxide per gram of starch, a mole to mole reaction between chlorine and base, and a temperature of 4° C. These conditions consistently gave starch pastes that were intermediate in glutinous character.

The effect of temperature on the oxidation was complex. First there was a general randomization of the internal

structure by a higher temperature. Also, there was a progressive degradation of the oxidized bonds by heat.

Starches that were milled without sulfur dioxide treatment were more resistant to oxidation than commercial cornstarches. About twice as much oxidant was required to obtain the same response from a starch that had not been treated with sulfur dioxide as was obtained from a commercial cornstarch.

The effect of sulfur dioxide on a native cornstarch was also established. Oxidation of these sulfur dioxide treated starches produced an effect similar to that obtained when a commercial cornstarch was oxidized.

The results of this study indicated that a controllable procedure for the oxidation was possible. However, the reaction involved a breaking of bonds in the starch granule to the extent that the reaction was objectionable. It also was determined that commercially milled cornstarches have undergone structural changes which may have adverse effects on their response to subsequent treatments.